

Desulfurization of thiophenes in oils into H<sub>2</sub>SO<sub>4</sub> using molecular oxygenChun Yang<sup>a,b</sup>, Hongwei Ji<sup>a,b</sup>, Chuncheng Chen<sup>a,b</sup>, Wanhong Ma<sup>a,b,\*</sup>, Jincui Zhao<sup>a,b,\*</sup><sup>a</sup> Key Laboratory of Photochemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, PR China<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100049, PR China

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## ABSTRACT

Because the reactivity of aromatic C–S bond is almost equal to that of hydrocarbon compounds of oils, it is difficult to convert thiophene and its derivatives into inorganic SO<sub>x</sub> using the current mild oxidative desulfurization (ODS) strategies for the production of clean fuels. Instead, they are generally transformed into sulfoxides and sulfones, which are not easily separated from fuel feedstock. Herein, we report an approach in which the commercially available heteropolyacid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in a CH<sub>3</sub>CN/iso-octane biphasic system can photocatalytically activate dioxygen to convert most thiophenic species to H<sub>2</sub>SO<sub>4</sub> (yield ~ 75%).

## 1. Introduction

Sulfur-containing compounds in fuels directly lead to the generation of exhaust gas and sulfate particulate matter, which are the main causes of acid rain and PM<sub>2.5</sub> production and seriously threaten the environment and public health [1]. The current industrial technique for desulfurization of fuels is catalytic hydrodesulfurization (HDS) based on transition metal sulfide catalysts, such as CoMo and NiMo [2]. Although HDS generally requires harsh conditions, such as high temperature, high pressure, and excessive H<sub>2</sub> consumption, the process can transform most organic sulfur into H<sub>2</sub>S, which can be readily separated and discarded (e.g., the well-known Claus method for regenerating and recovering elemental sulfur). Nevertheless, due to increased steric hindrance, the removal of these thiophene derivatives with *ortho*- or *para*-substituents such as 1- or 4-alkyl-substituted thiophenic derivatives and fused-ring aromatic compounds such as benzo- and dibenzothiophene is still quite difficult for the current HDS process [2]. These thiophenic species are some of the major immutable sulfur compounds present in general oils. Accordingly, the development of other effective desulfurization means, with a focus on conversion of these thiophenic derivatives, is highly desired. Examples of such processes include selective adsorption [3], extractive desulfurization [4], biodesulfurization [5], and oxidative desulfurization (ODS) [6–17]. Among them, ODS is a promising alternative because of its mild conditions, high reaction rate and no H<sub>2</sub> requirement. Encouragingly, because of the beneficial electron-donating effects of alkyl groups on the 1 and 4 positions of thiophenes, these intractable, bulky thiophenes are no longer immutable, as they are in HDS, but instead are very easily oxidized in ODS.

To date, various oxidative systems using oxidants such as molecular oxygen [6–11], hydrogen peroxide [12–15], *t*-butyl hydroperoxide [16], and ozone [17] have been tested. The current ODS processes, regardless of their catalyst or lack thereof, always have a fatal flaw, even when powerful oxidants are used, nearly all these systems convert these thiophenes to sulfoxides and sulfones instead of the desired inorganic sulfur products, SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [13,14,15] (Scheme 1a). Most sulfoxides and sulfones still need to be separated from the bulk oil phase, which results in difficult and tedious purification steps, making ODS mostly inferior to HDS. Very recently, a few of reports that demonstrate the oxidation of thiophenes in part into sulfate, based on the powerful oxidative species, such as OH free-radical which was formed from a MOF photocatalyst [10] or polyoxometalate thermal catalysis with high-pressure (20 bar O<sub>2</sub>) and temperature (120 °C) [11] (Scheme 1b). Despite the OH free-radical non-selectively attacking other hydrocarbons of oils that resulted in loss of fuels from such an obvious over-oxidation route, these studies showed that some catalyst frameworks containing molybdenum oxide or Mo-based polyoxometalate can perform other different activation route of the C–S bond of thiophenes to form sulfate instead of sulfoxides and sulfones.

We envision that mild fragmentation of the robust C–S aromatic bonds of thiophenic compounds and subsequent transformation to sulfate could be achieved through a concerted reaction strategy (Scheme 1c). That is, if a catalyst can selectively convert some of the thiophenes into the corresponding thiophenic aldehyde, rather than the more common sulfoxide and sulfone products, then the rest of the thiophenic species, acting as dienophiles, will undergo a thermodynamically favorable Diels-Alder [4 + 2] cycloaddition cascade in

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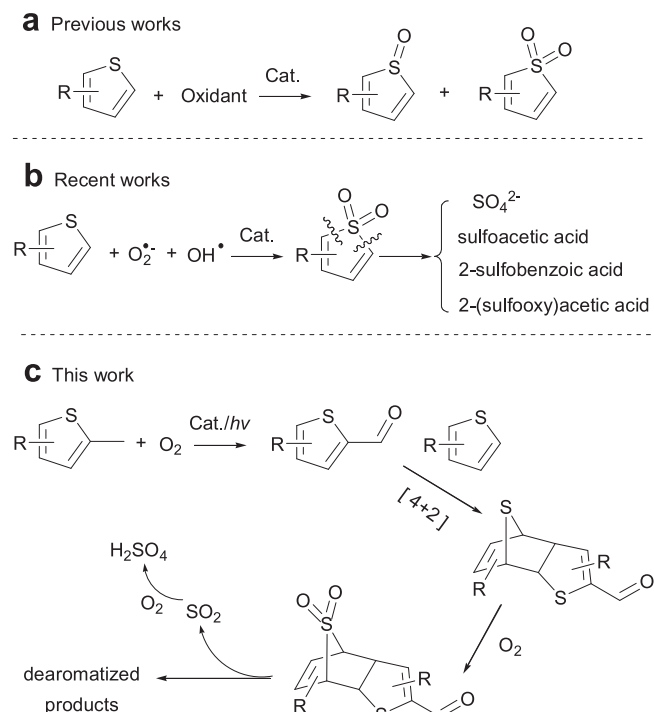
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**Scheme 1.** (a) Oxidation of thiophenes to sulfoxides and sulfones. (b) Oxidation of thiophenes to sulfate. (c) Cycloaddition reaction of the thiophenes and the thiophenic aldehyde to sulfate.

which the dearomatized S moiety will be readily oxidized to  $\text{SO}_2$  [14,18,19]. Relative to these indistinguishable oxidation mechanisms, the Diels-Alder reaction pathway should process under milder condition and be more selective for ODS.

To explore this concept, we performed a multitude of experiments using a photocatalytic system to complete the ODS reaction. A commercially available heteropolyacid,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , was selected as the catalyst because it can produce thiophenic aldehyde intermediate from alkyl-thiophene via dioxygen oxidation under UV excitation; a  $\text{CH}_3\text{CN}$ /iso-octane biphasic reaction system (BRS) was applied in which the  $\text{CH}_3\text{CN}$  phase was used to pre-dissolve the heteropolyacid photocatalyst and in situ extract thiophenes from the iso-octane phase for the ODS reaction, and the iso-octane was used as the simulated pure fuel phase. We attempt to provide an alternative desulfurization method to produce clean fuels from oils, especially for those are rich in the steric hindrance thiophenes.

## 2. Experimental section

### 2.1. Materials

All chemicals were purchased from commercial sources and were used without further purification unless otherwise noted. 2-Methylthiophene (2-MT), 2-ethylthiophene (2-ET), 3-methylthiophene (3-MT), 2,3-dimethylthiophene (2,3-DMT), 2,5-dimethylthiophene (2,5-DMT), thiophene (T), 2-thiophenecarboxaldehyde (2-TC), 2-thiophenecarboxylic acid (2-TA), 3-methylthiophene-2-carboxaldehyde, 2-sulfobenzoic anhydride,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , pyridine, chlorotrimethylsilane (TMSCl) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were purchased from Alfa Aesar. The partially dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was prepared by heating the commercial catalyst at  $200^\circ\text{C}$  for 10 h. 2-Acetylthiophene, 2,3,5-trimethylthiophene (2,3,5-TMT), and benzothiophene (BT) were purchased from J&K. Acetonitrile (ACN), iso-octane (IO), n-heptane, n-pentane, cyclohexane, 1-octene, 1,7-octadiene, benzene, toluene, cyclohexene, and styrene were all of analytical grade and were offered by

the Beijing Chemical Company. The  $\text{H}_2^{18}\text{O}$  ( $^{18}\text{O}$ : 98%) was purchased from Jiangsu Changshu Chemical, Limited. The  $^{18}\text{O}_2$  (97%) was purchased from Cambridge Isotope Laboratories, Inc. The real fluid catalytic cracking (FCC) gasoline samples were from Karamay or Guangxi Zhuang Autonomous Region.

### 2.2. General procedures

The photocatalytic oxidation reactions of model oil samples were conducted under the following conditions:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (10 mg, 0.6 mM) in 5 mL ACN; thiophenic compounds (0.1 mmol, 20 mM, 0.3%) in 5 mL IO; light source: 300 W Xe lamp equipped with infrared filters and a convex mirror to focus the light on the reaction vessel;  $\text{O}_2$ : 0.06 MPa; temperature:  $25 \pm 2^\circ\text{C}$ ; the samples were stirred for desired time.

The recycling tests were performed as follows: after a run was finished, the IO phase was separated, and then 5 mL of fresh IO containing thiophenic compounds (0.3%, w/w) was mixed with the original ACN phase for the next run (the system was not washed with  $\text{H}_2\text{O}$  for  $\text{H}_2\text{SO}_4$  extraction in these operations to maintain the maximum  $\text{H}_2\text{SO}_4$  accommodation).

Conditions for the desulfurization of real FCC gasoline experiments were as follows:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (60 mg, 0.6 mM) in 30 mL ACN was added to a 30-mL gasoline sample; after the photocatalysis, the mixture was extracted with 30 mL water; light source: 300 W Xe lamp equipped with infrared filters and a convex mirror to focus the light on the reaction vessel;  $\text{O}_2$ : 0.06 MPa; temperature:  $25 \pm 2^\circ\text{C}$ ; time: 48 h.

### 2.3. Analysis

Reaction samples from the two phases were analyzed after different irradiation times. Part of the ACN phase was silanized with 100  $\mu\text{L}$  HMDS and 50  $\mu\text{L}$  TMSCl in 1 mL anhydrous pyridine solution and then centrifuged to prepare it for gas chromatography-mass spectrometry (GC-MS) determination of sulfoxides, sulfones, small amounts of thiophene aldehydes, and thiophene acids. The conversion of 2-MT in the IO phase was determined directly by GC or GC-MS. Quantitative measurements of the conversion yield for thiophenic compounds in IO or ACN were determined by an Agilent 7890 A series gas chromatograph (GC) equipped with a flame photometric detector (FPD) and calibrated with an internal standard. An HP-5 capillary column (30 m  $\times$  0.25 mm  $\times$  2.5  $\mu\text{m}$ ) was used. The oven temperature was maintained at  $70^\circ\text{C}$  for 1 min, then increased by  $20^\circ\text{C}/\text{min}$  to reach  $100^\circ\text{C}$ , increased by  $10^\circ\text{C}/\text{min}$  to reach  $130^\circ\text{C}$ , held for 2 min, and increased by  $20^\circ\text{C}/\text{min}$  to reach  $250^\circ\text{C}$ . Gas chromatography-mass spectrometry (GC-MS) was carried out on an Agilent 7890 A series GC using an HP-5 MS capillary column (30 m  $\times$  0.25 mm  $\times$  2.5  $\mu\text{m}$ ) coupled with an Agilent 5977 A electron ionization mass spectrometer (EI-MS). The oven temperature was maintained at  $70^\circ\text{C}$  for 1 min, increased by  $20^\circ\text{C}/\text{min}$  to reach  $100^\circ\text{C}$ , increased by  $10^\circ\text{C}/\text{min}$  to reach  $130^\circ\text{C}$ , held for 2 min, increased by  $20^\circ\text{C}/\text{min}$  to reach  $250^\circ\text{C}$ , and held for 5 min.  $\text{H}_2\text{SO}_4$  production was quantified by a Dionex AERS 500 ion chromatograph (IC). The eluent for the IC was 25 mM KOH solution, and the flow rate was 1 mL/min.

The apparent quantum efficiency (AQE) was measured under irradiation by a 365 nm-LED (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China), which was used as a light source to trigger the photocatalytic reaction. The focused intensity and area of the light beam on the reactor for each 365 nm-LED were ca. 234  $\text{mW}/\text{cm}^2$  and 1  $\text{cm}^2$ , respectively. In this reaction,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (30 mg, 0.6 mM) and 2-MT (0.3 mmol, 20 mM, 0.3%) were in 15 mL ACN, the  $\text{O}_2$  pressure was 0.06 MPa, and the temperature was  $25 \pm 2^\circ\text{C}$ . The AQE was calculated according to eq.:

$$\text{AQE}(\%) = \frac{\text{number of reacted 2-MT}}{\text{number of incident photons}} \times 100.$$

Nuclear magnetic resonance (NMR)  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR spectra were

acquired on Bruker 300 MHz and 600 MHz spectrometers, respectively.  $^{31}\text{P}$  chemical shifts were referenced to external 85%  $\text{H}_3\text{PO}_4$ . The  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  high resolution mass spectrum (HRESI-MS) was collected on a Bruker Solarix 9.4 T. The thermogravimetric and differential thermal analysis (TG/DTA) were conducted from ambient temperature to 500 °C at a heating rate of 10 °C min $^{-1}$  under the flowing  $\text{N}_2$  and with a type Netzsch STA 409 PC thermal analyzer. Liquid chromatography-mass spectrometry (LC-MS) was performed with an Agilent 1200 HPLC system followed by an Agilent 6310 ion trap mass spectrometer using an ESI source in negative mode. LC conditions were as follows: A-water, B- 20 mM ammonium acetate and C-methanol; the detector wavelength was set to 210 nm. LC method: (for negative mode on MS) 0 min - 95% A and 5% B, 2 min - 95% A and 5% B, 35 min - 25% A, 5% B, and 70% C, 45 min - 25% A, 5% B, and 70% C, 46 min - 95% A and 5% B, 50 min - 95% A and 5% B.

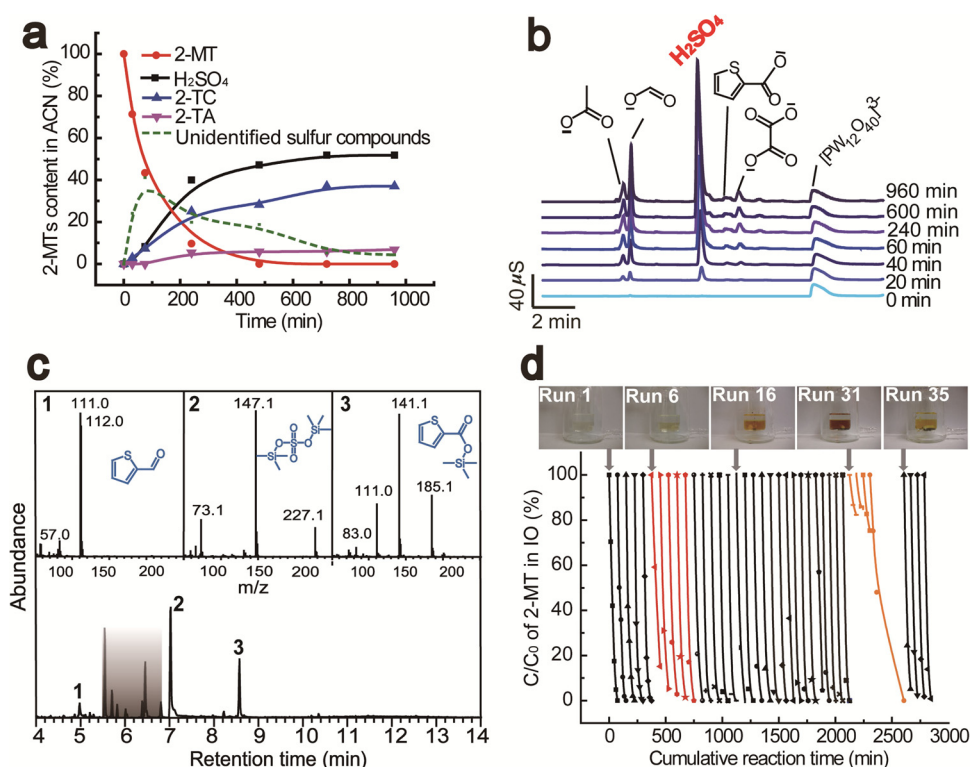
The total sulfur contents of the real gasoline samples were analyzed by a SINDIE 7039 monochromatic wavelength dispersive X-ray fluorescence spectrometer according to the NB/SH/T 0842–2010 standard test method.

### 3. Results and discussion

We first selected 2-methylthiophene (2-MT) as a representative member of the thiophenic family to undergo photocatalytic ODS (Fig. 1). In a typical photocatalytic ODS reaction, 0.1 mmol 2-MT was dissolved in 5 mL iso-octane (IO) (equivalent to 640 ppmw S) and 0.003 mmol  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  photocatalyst (equivalent to 3 mol% relative to the substrate 2-MT) was dissolved in 5 mL acetonitrile (ACN) and then the two solutions were mixed together to produce the BRS. In this BRS, 2-MT was photocatalytically oxidized mainly in the ACN phase with 0.06 MPa dioxygen. After 480 min of irradiation, the conversion of 2-MT was more than 99% (Fig. 1a). At this point, no remaining 2-MT was detected in the separated IO phase. Surprisingly, we did not detect the expected  $\text{SO}_2$  in the upper atmosphere of the reaction vessel or the common sulfoxides/sulfones in either phase after the full conversion of 2-MT. We posit that  $\text{SO}_2$ , if any, was at once oxidized to solubilized  $\text{H}_2\text{SO}_4$  in the ACN phase. In fact, we found that  $\text{SO}_2$  was easily oxidized

to  $\text{H}_2\text{SO}_4$  in our  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  photocatalytic system in the control experiments with  $\text{SO}_2$  as the substrate (Fig. S1a), while the other control experiments in  $\text{H}_2\text{O}$  without  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  shown  $\text{H}_2\text{SO}_3$  rather than  $\text{H}_2\text{SO}_4$  as the main product (Fig. S1b). Thus, we used GC-MS and ion chromatography (IC) to monitor the formation of  $\text{H}_2\text{SO}_4$  in the ACN phase (Fig. 1b,c) after 2-MT fully conversion, and the yield of  $\text{H}_2\text{SO}_4$  was quantified by IC (Fig. 1b). Indeed, the yield of  $\text{H}_2\text{SO}_4$  exceeded 50%. In addition to  $\text{H}_2\text{SO}_4$ , the other main sulfur-containing products (Fig. 1c) and sulfur-free products (Fig. 1c, Fig. S2a-d) were analyzed by GC-MS after silanization of the ACN phase. Peaks 1, 2, and 3 could be assigned to thiophene-2-carbaldehyde (2-TC),  $\text{H}_2\text{SO}_4$  (silanized), and 2-thiophene carboxylic acid (2-TA) (silanized), respectively, based on comparisons to standard samples (Fig. 1c). No sulfoxides or sulfones, which are the main intermediates in most reported ODS systems, were observed. In contrast, 2-TC was the major product after  $\text{H}_2\text{SO}_4$ , which was exactly an ideal intermediate to induce subsequent Diels-Alder reactions with other thiophene molecules. The total yield of the detected sulfur compounds reached 95.6% (see Table 1, entry 1). Although a fraction of sulfur-containing compounds could not be identified in the present photocatalytic system (no more than 4.4%), these compounds were confirmed to not be sulfoxides or sulfones. Synchronously, the carbon mass balance results (Table S1) of the 2-MT had shown that, of the hydrocarbon component of the 2-MT, a part of carbon was mineralized to  $\text{CO}_2$  (~27.5%), 72% or more were small molecule carboxylic acids. These polar by-products that were left behind in the ACN phase and separated from oil phase could be used elsewhere [6–8].

















The increase of reaction temperature from 50 °C to 70 °C when irradiated with light could significantly shorten the 2-MT conversion time, but meanwhile produced higher proportion of the 2-TC from approximately 60% to 80% (Fig. S3). Control experiments without  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  or light irradiation showed that the conversion of 2-MT was less than 3% after 150 min (Fig. S4a), indicating that the ODS reaction was neither a simple photolysis nor a thermal catalytic reaction. This preliminary result showing the formation of 2-TC thereby resulting in  $\text{H}_2\text{SO}_4$  rather than sulfoxides or sulfones, demonstrates the attractiveness of this reaction system.



**Fig. 1.** (a) Photocatalytic conversion of 2-MT in the BRS and the formation of  $\text{H}_2\text{SO}_4$ , 2-TC, and 2-TA in ACN versus irradiation time. (b) IC chromatograms of the ACN phase from the case of (a). (c) GC-MS spectra of the oxidation products of 2-MT (below). The peaks of 1, 2 and 3 correspond to the sulfur-containing products, while the peaks in the gray shaded region correspond to the sulfur-free products. The EI-MS spectra of sulfur-containing products 1–3 were recorded after silanization (top). (d) 38 runs for recycling tests for 2-MT oxidation (fed 0.3% at a run) by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.6 mM) catalyst in the BRS. The five photographs on the top show the colors of the BRS prior to different runs.

**Table 1**

Oxidation of various thiophenic compounds (640 ppmw S) in the photocatalytic oxidative BRS.

Entry	Substrate	Conv. (%)	Main sulfur-containing products (yields, %) <sup>a</sup>	
			H <sub>2</sub> SO <sub>4</sub>	Other sulfur-containing products
1		> 99.9	51.8	 (37), 
2		> 99.9	52.9	 (6.8),  (18.2)
3		> 99.9	63.8	 (7.4)
4		> 99.9	71.3	–
5		> 99.9	75.4	–
6		70.9	55.0	–
7		74.3	22.5	 (46.3)
8		17.6	9.3	–
9		> 99.9	1.4	 (97)

<sup>a</sup> The main sulfur-containing products were determined by GC–MS and quantified by IC (H<sub>2</sub>SO<sub>4</sub>) or GC–FPD (other products).

After the initial success of using 2-MT as the model thiophenic compound, we investigated the ODS of as many members of the thiophenic family that are commonly found in gasoline as possible using our BRS. The results showed that most of the starting thiophenic compounds could be converted (> 99%) in less than 150 min under identical experimental conditions; the exceptions were 3-MT, benzothiophene (BT), and T (Table 1, Fig. S5). Of the main sulfur-containing products, H<sub>2</sub>SO<sub>4</sub> was the dominant ODS product with a maximum yield of 75.4% in the ODS of 2,3,5-trimethylthiophene (2,3,5-TMT) (Table 1 and Fig. S2e–l). To our knowledge, this sulfate yield was the highest among ODS examples reported. This universal tendency of S from different substituted parent thiophenes to be converted to H<sub>2</sub>SO<sub>4</sub> indicated that H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was capable of cleaving aromatic C–S bonds to produce inorganic H<sub>2</sub>SO<sub>4</sub>. Although the individual conversions of 3-MT, BT, and T were much lower than those of thiophenes with alkyl substituents at other positions (such as 2-MT), we found that when any one of the immutable 3-MT, BT, and T species or all three were mixed with other thiophenes with alkyl substituents at other positions (such as 2-MT) in ACN, the conversion under identical conditions dramatically increased compared to that of 3-MT, BT, or T alone (Fig. S6a). This synergistic effect allowed the conversion of the immutable thiophene components without the pre-addition of other substituted thiophenes because actual fuels contain a large enough variety of thiophenes to create such an effect.

We tested different initial concentrations of 2-MT, 0.3%, 3%, 30%, and 60% (w/w) in the IO of the BRS to examine the turnover number (TON) of the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> photocatalyst; the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> content was always 0.25% (w/w) in the ACN phase. In the case of 60% (w/w), the total concentration of S was as high as 4.2 M (versus 0.6 mM H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), giving a remarkable TON of 6881 (Fig. S7). The apparent quantum efficiency (AQE) was approximately 2.47% when H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was illuminated by 365 nm monochromatic light.

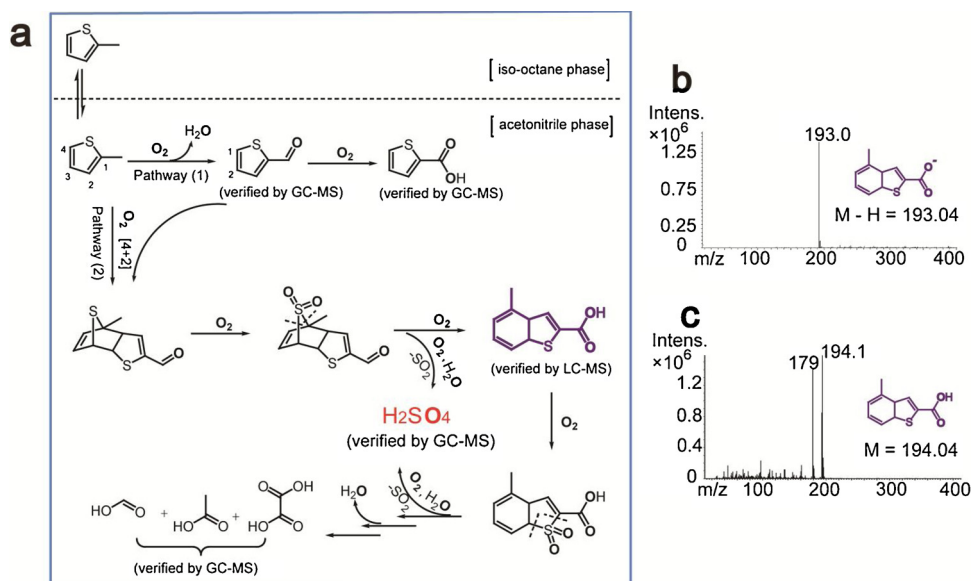
We then conducted recycling tests to examine the reusability of the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> photocatalyst as well as the two phases. There was no significant decrease in the activity of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> after being recycled 5 times (Fig. 1d). However, when we examined the ACN phase after an overnight reaction, we found that the colorless ACN phase had become light yellow (Run 6), which was attributed to the buildup of 2-TC in the

ACN phase. As the number of cycles increased, the ACN phase became darker in color, and the accumulation of 2-TC became significant (Run 16). After letting the ACN phase rest for several days (after Run 30), it became brown presumably due to the polycondensation of 2-TC. Nevertheless, the conversion rate of fresh batches of thiophene could be maintained at the original level by simply continuing recycling 4 runs (from Run 31 to Run 34). Therefore, even without frequent switching to a fresh or purified batch of ACN, the efficiency of sulfur removal remained satisfactory under these conditions in our BRS. It is worth emphasizing that although H<sub>2</sub>SO<sub>4</sub> yield reached only around 50–75% within one cycle of completely converting thiophenes, the rest sulfur-containing compounds (the major components was TC) and unidentified constituents (less than 4%) migrate into the ACN phase and gradually convert into H<sub>2</sub>SO<sub>4</sub> over the later course. After separating the ACN phase (the bottom layer of the system), we could obtain an ACN-free IO phase by washing only once with an equal volume of water (Fig. S4 e–h).

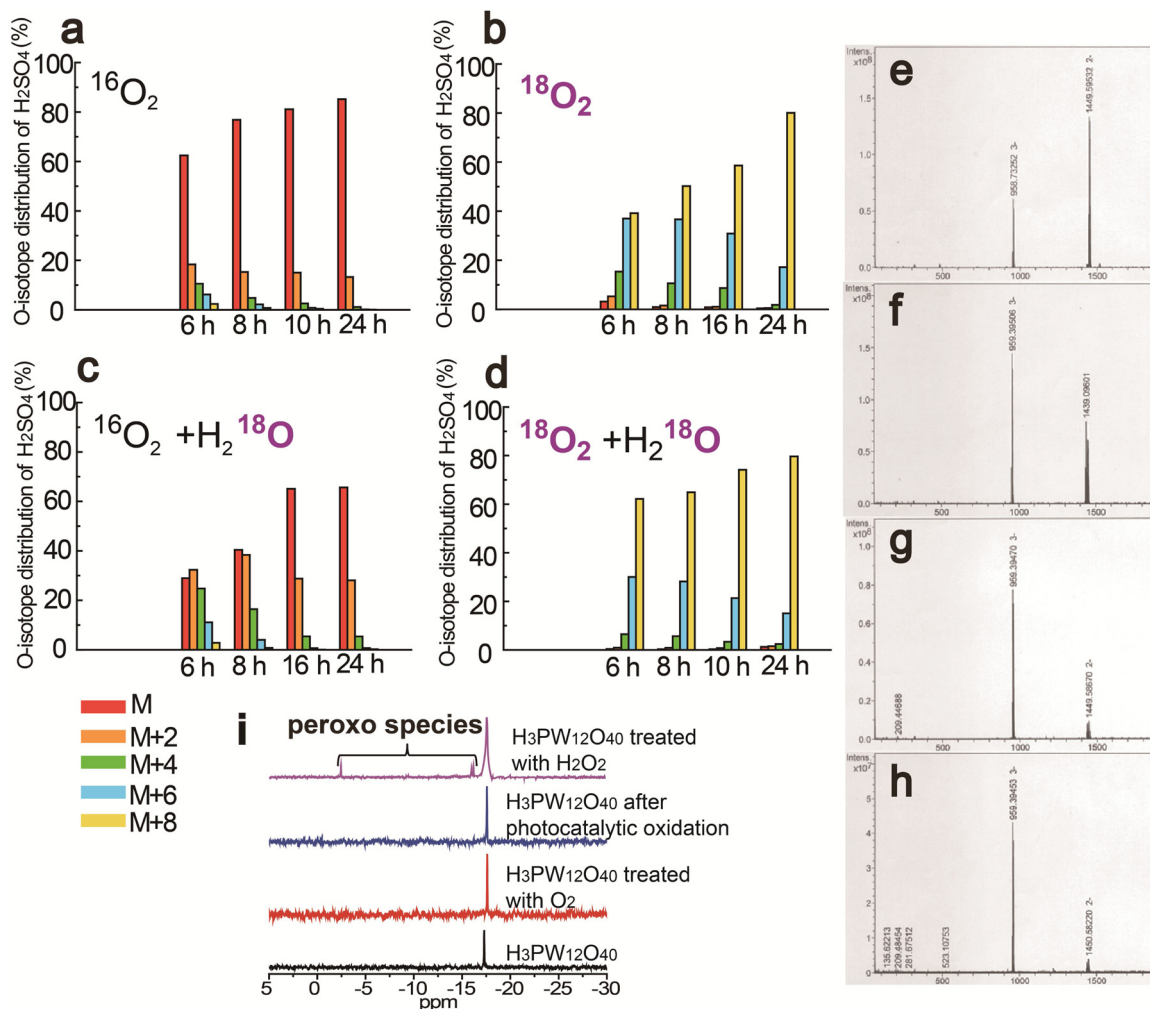
We selected several alkanes, olefins, and aromatic hydrocarbons to investigate which components in the real liquid fuels would inhibit the efficiency of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> for the ODS of thiophenes in this system. The results revealed that some olefins do effect the removal of 2-MT to an extent (Fig. S8). Then, the system was applied to two actual FCC gasolines, Karamay FCC gasoline and Guangxi (China) FCC gasoline, after undergoing rigorous HDS treatment (Table S2). The initial total sulfur concentration in Karamay FCC gasoline was approximately 89 ppmw, and only 20 ppmw remained after photocatalytic oxidation. For Guangxi FCC gasoline, the sulfur concentration was reduced from 70 ppmw to 24 ppmw. With other identical conditions to the photocatalytic treatments, the control experiments without light irradiation (Blank A in Table S2) and without catalyst H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Blank B in Table S2) both shown very low removal rates of sulfur. This demonstrated that it was only the excited H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> to play the role in our ODS treatments.

We next confirmed that the formation and accumulation of the intermediate 2-TC from the alkyl-substituted thiophenes mediated by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> promoted fast desulfurization of immutable thiophenes, including non-substituted T and 3-MT. When we mixed T or 3-MT with 2-TC in the presence of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> BRS, the reaction rate of mixed T was twice that of T alone, and the reaction rate of mixed 3-MT was 6.7 times faster than that of 3-MT alone (Fig. S6b). Even when we mixed 2-MT with 2-TC in the presence BRS, we found that the rate of conversion of 2-MT was substantially faster than that of 2-MT alone under otherwise identical conditions (Fig. S4b). The control reaction with the desulfurization product of dibenzothiophene was sulfone instead of H<sub>2</sub>SO<sub>4</sub> showed that dibenzothiophene could not undergo Diels-Alder addition (see Table 1, entry 9). These results strongly indicate that 2-TC, the stable intermediate resulting from MT oxidation, is the key intermediate in the conversion of all the studied thiophenes, including the most obstinate, unsubstituted thiophenes. We then considered how TC accelerated the facile conversion of these thiophenes to H<sub>2</sub>SO<sub>4</sub>. As mentioned above, during the conversion of 2-MT, the sum of the quantities of 2-TC, 2-TA, and H<sub>2</sub>SO<sub>4</sub> was not equal to the quantity of converted 2-MT at any point in the reaction; this deviation was initially large but then decreased with increasing reaction time, as shown by the broken line in Fig. 1a (~ 4% lack finally). For analyzing these unascertained intermediates at the time of their maximum concentrations that determined through continuous sampling, the strongest molecular ion peak from the reaction with 2-MT and 2-TC as reactants was at *m/z* 193.0 in LC–MS spectra, (Fig. 2b), and when analyzing the same sample using GC–MS, the strongest molecular ion peak was at *m/z* 194.1 (Fig. 2c). This peak was readily assigned to a product of the further oxidation of the cycloaddition product (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S, [M–H] = 193.04, [M] = 194.04) via a concerted path. Among all the components, this sulfur-containing compound was very vital in elucidating both the concerted path and the cleavage of aromatic sulfur to produce H<sub>2</sub>SO<sub>4</sub>. The six-membered ring formation and dearomatization of thiophene





**Fig. 2.** (a) Proposed desulfurization mechanism for the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  photocatalytic oxidation of 2-MT in the BRS along key Diels-Alder cycloaddition route. LC-MS (b) and GC-MS (c) spectra of the further oxidation of the cycloaddition product formed from 2-MT and 2-TC.



**Fig. 3.** (a-d) Oxygen-isotope distribution of  $\text{H}_2\text{SO}_4$  versus irradiation time for the ODS of 2-MT (200 mM). (a & b) hydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.6 mM) and (c & d) partially dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.6 mM) with the addition of  $\text{H}_2^{18}\text{O}$  (10 mg, 100 mM). In the histograms, M, M + 2, M + 4, M + 6, and M + 8 denote X = 0, 1, 2, 3, and 4 in  $\text{S}^{16}\text{O}_{(4-X)}^{18}\text{O}_X^{2-}$ . HRESI-MS spectra of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (e) before and (f-h) after photocatalytic oxidation: (f)  $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$  ( $\text{H}_2^{16}\text{O}$  from the catalyst hydrate); (g)  $^{18}\text{O}_2 + \text{H}_2^{16}\text{O}$  ( $\text{H}_2^{16}\text{O}$  from the catalyst hydrate); and (h)  $^{18}\text{O}_2 + \text{H}_2^{18}\text{O}$  ( $\text{H}_2^{18}\text{O}$  extrinsically added). (i)  $^{31}\text{P}$  NMR spectra of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  under various conditions.  $[\text{H}_2\text{O}_2]/[\text{W}] \approx 7:1$ .  $\text{D}_2\text{O}$  was added in all sample solutions at a  $\text{D}_2\text{O}/\text{sample}$  ratio of 1:3 before measurement.

must result from the Diels-Alder addition of two five-membered ring compounds [14,18,19]. In other words, as expected, a Diels-Alder reaction occurred between the thiophene and 2-TC in a concerted manner (Fig. 2a). Once the thiophenes were converted into non-aromatic sulfur species, the aliphatic C–S bond was easily broken to produce  $\text{SO}_x$ , which was quickly oxidized to  $\text{H}_2\text{SO}_4$ .

We then sought to clarify the role of dioxygen in the oxidation of the C–S bonds of thiophenes to produce  $\text{H}_2\text{SO}_4$  by using labeled  $^{18}\text{O}_2$  and  $\text{H}_2^{18}\text{O}$ . Different from natural  $\text{O}_2$  isotope conditions (Fig. 3a) [20], when 18-oxygen labeled  $^{18}\text{O}_2$  (97%) under otherwise identical conditions to the general experiment, we observed nearly the same amounts of  $\text{S}^{18}\text{O}_4^{2-}$  [M + 8] and  $\text{S}^{16}\text{O}^{18}\text{O}_3^{2-}$  [M + 6] after 6 h of photocatalysis (Fig. 3b). With extending the irradiation time, [M + 8] reached approximately to 80% at 24 h, which was slightly lower than the value calculated based on 97% 18-oxygen abundance in the initial  $^{18}\text{O}_2$ , 88.5%. These results signified that most of the oxygen in the final  $\text{H}_2\text{SO}_4$  species came directly from dioxygen. The residual proportion of the oxygen (16-oxygen) was derived from the effect of crystal water ( $\text{H}_2^{16}\text{O}$ , 0.066 mM) of the hydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [21], which was incorporated into  $\text{S}^{16}\text{O}^{18}\text{O}_3^{2-}$  via exchange between  $\text{S}^{18}\text{O}_4^{2-}$  and  $\text{H}_2^{16}\text{O}$  (the exchange control experiments between  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  as shown in Fig. S10). To support this, we conducted further control experiments to confirm that the exchange effect is the source of the lack of isotopic purity of the oxygen. We performed the experiment by using partially dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (Fig. S9b) as the photocatalyst (Fig. 3c) and the addition of excess  $\text{H}_2^{18}\text{O}$  (100 mM) [22]. The results of the experiment ( $^{16}\text{O}_2$  + added  $\text{H}_2^{18}\text{O}$ ) were consistent with our prediction, in which  $\text{S}^{16}\text{O}_4^{2-}$  [M] was the major component after 24 h reaction (Fig. 3c), and the proportion of  $\text{S}^{16}\text{O}_3^{18}\text{O}^{2-}$  [M + 2] was significantly higher than when  $^{16}\text{O}_2$  was used without added  $\text{H}_2^{18}\text{O}$  (Fig. 3a), which was due to the exchange between  $\text{S}^{16}\text{O}_4^{2-}$  and  $\text{H}_2^{18}\text{O}$ . Similarly, the results of the experiment with  $^{18}\text{O}_2$  + added  $\text{H}_2^{18}\text{O}$  (Fig. 3d) compared to those of Fig. 3b were also consistent with  $\text{H}_2\text{O}$  exchange with  $\text{H}_2\text{SO}_4$ . To determine if the dioxygen was steadily incorporated into the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  photocatalyst during the ODS process, we characterized  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  before and after the reaction under the various isotope conditions by negative-ion high-resolution mass spectrometry (HRESI-MS) in the ACN solution. Two base peaks were observed at  $m/z$  959.07 (assigned to  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ) and  $m/z$  1449.59 (assigned to  $[\text{HPW}_{12}\text{O}_{40}]^{2-}$ ) before the photocatalytic reaction (Fig. 3e). The HRESI-MS spectrum of the ACN phase showed that the two peaks did not shift (Fig. 3f–h), although the relative intensity of the two peaks changes based on the initial amount of  $\text{H}_2\text{O}$  and the generated sulfuric acid. In addition, no new peaks were detected in the  $^{31}\text{P}$  NMR spectrum of the sample using  $\text{O}_2$ -treated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , as shown in Fig. 3i, while two new peaks appeared in the  $^{31}\text{P}$  NMR spectrum of the sample using  $\text{H}_2\text{O}_2$ -treated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (Fig. 3j). These results clearly indicate that the O atoms of both dioxygen and  $\text{H}_2\text{O}$  were not exchange or incorporated into  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  to generate the polyoxoperoxo species and then inserted into the thiophene species to form sulfone and sulfoxide. This insertion mechanism is well known in thermocatalysis and involves  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $\text{H}_2\text{O}_2$  acting as the oxidant [23,24].

#### 4. Conclusion

An approach in which commercially available heteropolyacid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  in a  $\text{CH}_3\text{CN}$ /iso-octane two-phase medium can photocatalytically activate dioxygen to split most thiophenic members (conversion > 99%) into  $\text{H}_2\text{SO}_4$  (yield > 75%) through the formation of crucial thiophenic aldehyde intermediates, whereby most of the thiophenic species undergo Diels-Alder cycloaddition and are thereby dearomatized and oxygenated to produce  $\text{H}_2\text{SO}_4$ . The resulting oxidation products (including  $\text{H}_2\text{SO}_4$ , thiophenic aldehydes, acids, etc.) prefer to migrate to the  $\text{CH}_3\text{CN}$  phase, and the iso-octane phase can be separated as sulfur-free clean fuel. The  $\text{CH}_3\text{CN}$  phase can be repeatedly used over at least 38 runs. We used isotopic 18-oxygen-labeled  $\text{O}_2$  and

$\text{H}_2\text{O}$  to analyze the oxygen profile of the  $\text{H}_2\text{SO}_4$  product as well as  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , which revealed a closed polyacid anion catalytic route that avoids the oxidative formation of sulfoxides and sulfones. This strategy could potentially be extended to the mild desulfurization of actual gasolines using  $\text{O}_2$ .

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.04.076>.

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